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NEW STRATEGIES FOR DESIGNING RECEPTORS AND PREPARING ULTRA-SENSITIVE, CHEMICALLY SELECTIVE ELECTRODE SURFACES		F49620-00-1-0230		
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13. ABSTRACT (Maximum 200 words) Our research efforts have been focused on the design and synthesis of macrocyclic complexes based on the "Weak-Link Approach" and their applications for recognition and separation technologies. Several important research discoveries have been made over the course of the project. A more thorough understanding of the fundamental parameters that control the formation of macrocyclic receptors formed via the Weak-Link Approach has been developed. In addition, novel hemilabile ligands that have used to form a new class of macrocycles referred to as "molecular tweezers" have been designed. These structures can recognize molecule based on size, shape and the ability to form π-stacking interactions. Using the Weak-Link Approach we have also synthesized a stable Rh(II) species, a set of chiral macrocyclic receptors and a series of heterobimetallic macrocyclic structures. This provides us with a library of compounds to investigate in future sensing applications. In the area of signal transduction, we have developed several fluorescent systems that utilize a new class of highly fluorescent ligands and Fluorescence Resonance Energy Transfer (FRET). Their receptor and molecular sensing properties have been investigated.				
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Final Report – (3/15/00 – 11/30/02)

for Grant: F49620-00-1-0230

New Strategies for Designing Receptors and Preparing Ultra-Sensitive, Chemically Selective Electrode Surfaces

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August 31, 2003

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II. OBJECTIVES

The principle aims of this research effort are:

1. To design a new class of inorganic, macrocyclic receptors for detecting analytes of interest to the DoD;
2. To design new methods of signal transduction based upon two-component, current rectifying, self-assembled monolayers on electrode surfaces; and
3. To provide research opportunities to City Colleges of Chicago minority undergraduates.

These objectives are unchanged from the original proposal.

III. STATUS OF WORK

Over the lifetime of this grant, seven Harold Washington College (HWC) minority undergraduate students were funded and pursued research jointly with Northwestern University faculty, post-doctoral associates and graduate students. All of these students have matriculated from HWC. Donald Cheatem is enrolled in the Medical School at the University of Illinois-Chicago; Gerri Hutson is pursuing a Chemistry Major at Northern Illinois University; Francisco Ruiz has entered the workforce; Albert Adebayo has completed a bioengineering technical program at Harry S. Truman College; Jacqueline Romero is enrolled in the Engineering School at the University of Illinois-Chicago; Suzanne Arguijo is enrolled in the Engineering School at the DePaul University; Arturo Ospina is enrolled in the College of Arts and Sciences at Northwestern University.

Four Northwestern Graduate Students and two Northwestern Post-Doctoral Associates were also supported with these funds. Adam Eisenberg's research efforts focused on the design and synthesis of heterobimetallic macrocyclic complexes via the "Weak-Link Approach". Mr. Eisenberg successfully defended his Ph.D. thesis in August 2002 and is currently a postdoctoral fellow with Professor Milan Mrksich (University of Chicago).

Felicia Dixon's contributions included design, synthesis and investigation of Rh(II) complexes featuring a piano-stool geometry and synthesis of chiral macrocyclic complexes via the "Weak-Link Approach" and investigations of their molecular recognition and sensing properties. Ms. Dixon successfully defended her Ph.D. thesis in August 2002 and is currently a research scientist position at L'Oreal Hair Research Center (Chicago, IL).

Khalid Salaita's research was aimed at the preparation of chemically sensitive electrode surfaces using Dip-Pen Nanolithography (DPN). Mr. Salaita continues progress towards a doctoral degree in Professor Mirkin's group.

Dr. You-Moon Jeon investigated the molecular recognition properties of chiral macrocyclic receptors. Currently, Dr. You-Moon Jeon is employed by LG, Corporation (Korea).

Dr. Ovchinnikov synthesized a new class of three-fold symmetric, ligand-dissymmetric and fluorescent macrocyclic complexes and investigated their receptor and molecular sensing

properties. Currently, Dr. Ovchinnikov continues his postdoctoral appointment in Professor Mirkin's group.

Our research efforts have been focused on the design and synthesis of macrocyclic complexes based on the "Weak-Link Approach" and their applications for recognition and separation technologies. Several important research discoveries have been made over the course of the project. A more thorough understanding of the fundamental parameters that control the formation of macrocyclic receptors formed via the Weak-Link Approach has been developed. In addition, novel hemilabile ligands that have used to form a new class of macrocycles referred to as "molecular tweezers" have been designed. These structures can recognize molecule based on size, shape and the ability to form π -stacking interactions.

Using the Weak-Link Approach we have also synthesized a stable Rh(II) species, a set of chiral macrocyclic receptors and a series of heterobimetallic macrocyclic structures. This provides us with a library of compounds to investigate in future sensing applications. In the area of signal transduction, we have developed several fluorescent systems that utilize a new class of highly fluorescent ligands and Fluorescence Resonance Energy Transfer (FRET). Their receptor and molecular sensing properties has been invistgated.

Finally, we have begun exploring how Dip-Pen Nanolithography (DPN) can be used to write multi-component features on an electrode surface and how feature size can be tailored using electrochemistry.

IV. ACCOMPLISHMENTS/NEW FINDINGS

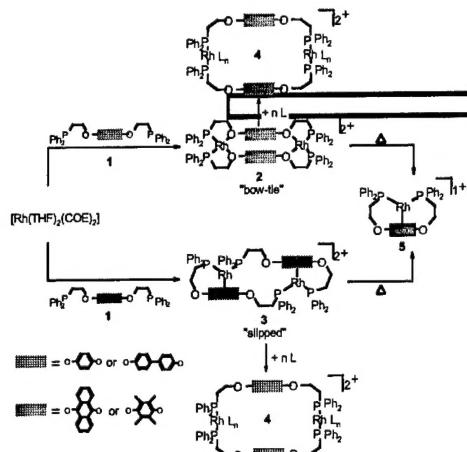
A formal undergraduate research program between HWC, a two-year, primarily minority institution, and NU, a major research university, was established and developed as a result of this project. This program allows talented and motivated minority undergraduates from HWC to pursue an individual research project using state-of-the-art facilities at NU. Without such a partnership, HWC would not be able to provide a comparable experience for its students.

New Sensors via the Weak-Link Approach.

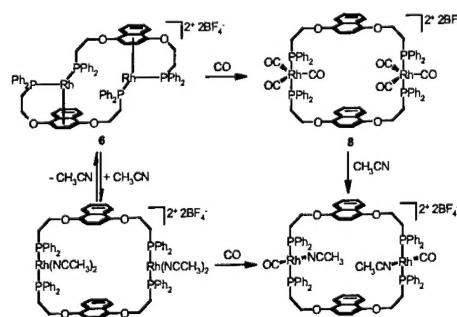
The Mirkin Group has pioneered the development of the Weak-Link Approach, which allows one to construct flexible binuclear macrocyclic and polynuclear three-dimensional cage architectures from hemilabile ligands and metal precursors. These macrocycles and cage systems can be used as receptors for the basis of chemical sensors. The approach utilizes hemilabile ligands **1** to organize metal centers in the form of rigid condensed intermediates (**2** and **3**) with intentionally designed strong and weak metal links, Scheme 1. These structures can be subsequently opened into flexible macrocycles **4** through high yielding, small-molecule ligand substitution reactions, which break the weak links but not the strong ones. For the systems studied thus far, two distinct structural isomers of the condensed intermediate, descriptively termed the “bow-tie” and “slipped” intermediates (**2** and **3**, respectively), have been characterized; they differ in the bonding modes of the metal centers to the hemilabile ligands used. Moreover, these binuclear structures are the kinetic products of the reactions used to form them with the thermodynamic products being mononuclear piano-stool complexes **5**, Scheme 1.

We have also designed and synthesized a new naphthalene-based hemilabile ligand that allows us to systematically examine some of the important factors that control the formation of both condensed intermediates as well as the thermodynamic mononuclear products, Scheme 1. The motivation for synthesizing the naphthalene-based ligand comes from the observation of the reaction pathways for related ligands based on phenyl, biphenyl, anthracenyl, and durenyl moieties. In the case of Rh(I) when phenyl- or biphenyl-based phosphinoalkylether ligands were used, the slipped intermediates (binuclear Rh(I) structures which have two-legged piano-stool geometries with η^6 -arenes and bis(phosphine)-Rh(I) bonds) are the predominant products. However, when the durenyl- or anthracenyl-based ligands were used, the bow-tie intermediates are the predominant products under virtually identical conditions. Since naphthalene is the intermediate structure between phenyl and anthracenyl, it is interesting to study the tendency of the naphthalene-based ligand to form either the bow-tie or condensed intermediate. In addition, due to the dissymmetry of the naphthalene-based ligand, one can study the possibility and preference for *syn* or *anti* metalallocyclopanes. Finally, we have used this ligand and complexes formed from it to map out some of the factors that control the conversion of the condensed intermediates into the mononuclear thermodynamic products.

We have successfully prepared binuclear and



Scheme 1



Scheme 2

mononuclear rhodium macrocycles **7-11** based on the parent dissymmetric 1,4-bis(2-diphenyl phosphinoethoxy) naphthalene macrocycle **6**, Scheme 2, that are fully characterized by various means including X-ray crystallography. The reactivity of the condensed intermediate is similar to other Rh(I) complexes prepared in the group towards incoming ligands such as carbon monoxide and acetonitrile (Scheme 2). However, the facile and clean conversion of binuclear intermediate **6** into the mononuclear product **10** is novel reactivity to date, Scheme 3.

The slipped binuclear intermediate **6** and mononuclear Rh(I) complex **10** have η^4 -arene-Rh(I) interactions in the solid state. We have used this reaction to study the process of conversion from binuclear to mononuclear complexes under various conditions including the presence and absence of coordinating solvents. We have found that the conversion of **6** to the monomeric Rh(I) complex **10** is accelerated by weakly coordinating solvents such as THF, however the strongly coordinating solvent, acetonitrile, retards the conversion significantly. Finally, the weak arene-Rh(I) bond of the monomeric Rh(I) complex **10** was selectively cleaved via the coordination of CO and CH_3CN in *trans* fashion which form a new open mononuclear macrocycle **11**, Scheme 3.

Unusual Rh(II) Complexes with Hemilabile Ligands. Our group has also been interested in the stabilization of mononuclear Rh(II) metal center in a two-legged piano-stool geometry utilizing phosphinoalkylaryl hemilabile ligands. We designed and synthesized the hemilabile ligand, 1,4-bis[4-(diphenylphosphino)butyl]-2,3,5,6-tetramethylbenzene, which has been used to synthesize the most stable Rh(II) complex, $[(\eta^6\text{-}1,4\text{-}bis[4\text{-}(diphenylphosphino)butyl]\text{-}2,3,5,6\text{-}tetramethylbenzene})\text{Rh}][\text{PF}_6]$ (12) (Figure 1), studied to date.

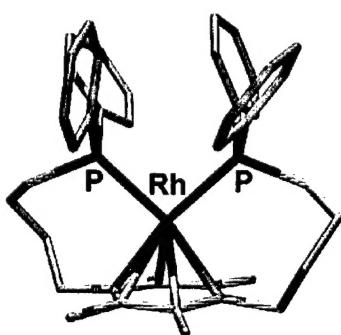
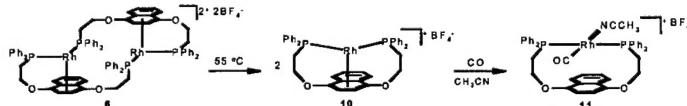
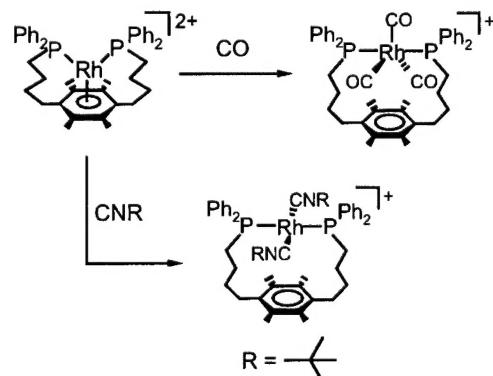


Figure 1. X-Ray structure of complex **12**.



Scheme 3



Scheme 4. Reactivity of Rh(II) complex **12** with CO and CH_3CN .

Electrochemical and structural properties of complex **12** were investigated. We studied the paramagnetic properties of complex **12** in solution using EPR spectroscopy, which exhibited *g*-values consistent with the formation of Rh(II).

Significantly, we also studied the reactivity of this unusual Rh(II) complex in the presence of small molecules such as CO and CH₃CN. In the presence of each of these ligands the Rh(II) complex was reduced to its Rh(I) form and subsequently reacted to form various Rh(I) complexes (Scheme 4). The mechanistic aspects of these reactions are currently under investigation.

Chiral Macroyclic Receptors via the Weak-Link Approach. We have developed a new class of hemilabile ligand that complexes transition metals to form molecular tweezers, Figure 2. These structures have been designed to recognize analyte molecules in multiple ways: 1) shape, 2) hydrophobicity, 3) size, 4) ligation to the metal, and 5) π -stacking between guest and host. They are ideally suited for recognizing functionalized aromatics such as TNT.

We have demonstrated that chiral backbones could be incorporated into hemilabile ligands in order to synthesize chiral macrocycles. The chiral group gives the ligand a pincer-type geometry capable of binding one metal center. Mononuclear macrocycles are formed via reaction with small molecules that preferentially bind to the metal center subsequently breaking the weak metal-ether bonds. Our initial studies have focused on incorporating the chiral group 1S,2S-cyclohexanediol into the ligand system. Upon reaction with a Rh(I) starting material, the condensed intermediate **13**, can be obtained (Figure 3). Weakly metal binding ether linkages were immediately exchanged with gaseous CO, and the open state of macrocycles **14** was obtained, Figure 4. The chiral recognition properties of the complex **14** were studied by reacting with biologically active chiral molecules such as mandelonitrile, cinchonine, styrene oxide and amino acids. The host molecule **14** differentiated stereoisomers of mandelonitrile forming diastereomeric complexes. In addition, we applied another method for synthesizing approach to chiral macrocycles (Scheme 5). A binding site of a macrocycle was converted to one with chiral cavity by self-assembling chiral building blocks to metal centers. These results provide not only advanced synthetic methodologies for chiral

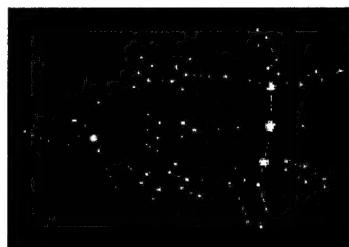


Figure 2. A “molecular tweezer” capable of binding nitroaromatics. The aromatic groups of the tweezer help guide the molecule into the macrocyclic cavity.

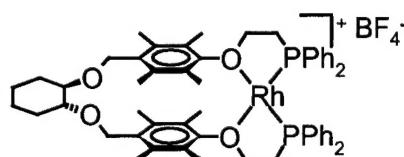


Figure 3. Complex 13.

Weakly metal binding ether linkages were immediately exchanged with gaseous CO, and the open state of macrocycles **14** was obtained, Figure 4. The chiral recognition properties of the complex **14** were studied by reacting with biologically active chiral molecules such as mandelonitrile, cinchonine, styrene oxide and amino acids. The host molecule **14** differentiated stereoisomers of mandelonitrile forming diastereomeric complexes. In addition, we applied another method for synthesizing approach to chiral macrocycles (Scheme 5). A binding site of a macrocycle was converted to one with chiral cavity by self-assembling chiral building blocks to metal centers. These results provide not only advanced synthetic methodologies for chiral

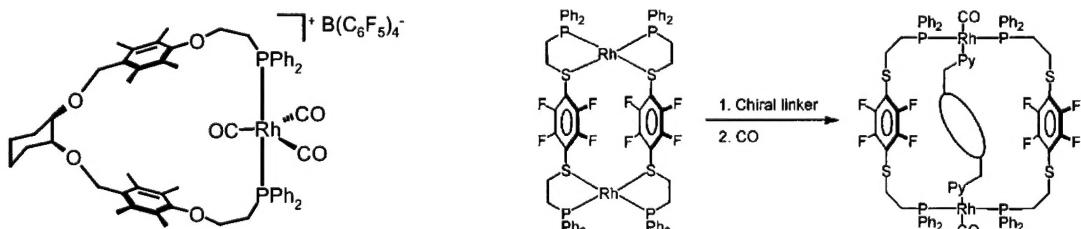
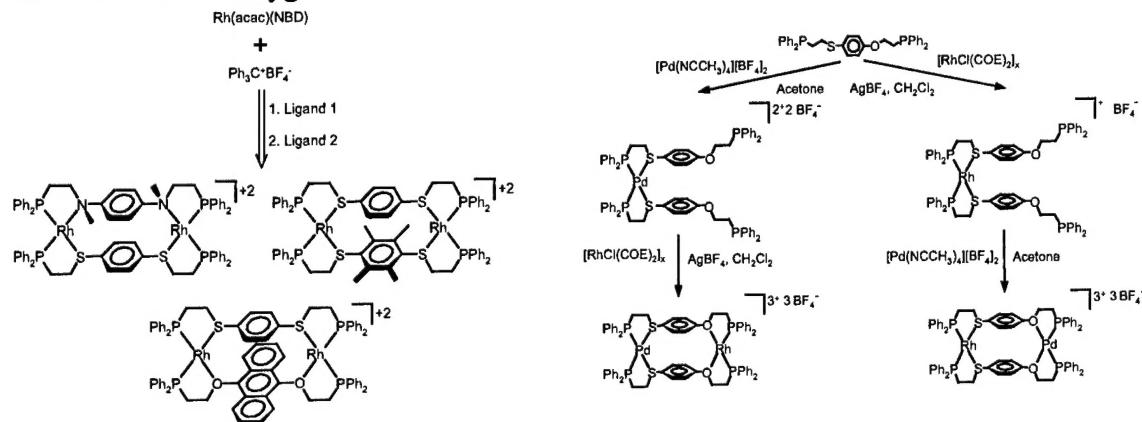


Figure 4. Chiral molecular tweezer **14**.

Scheme 5. Self-Assembly of chiral macrocycle.

macrocyclic complexes and a basic understanding of chiral molecular recognitions but they are also useful tools for analyses and separations of biologically active and hazardous chemicals.

Ligand-Dissymmetric and Heterobimetallic Macrocycles Synthesized via The “Weak-Link Approach”. The “Weak-Link Approach” also enables one to use hemilabile organic ligands to construct large macrocyclic architectures in nearly quantitative yields. In order to expand the scope of applications of this research project and to gain a fundamental knowledge on how hemilabile ligands predefine the formation of these macrocyclic structures, we have developed strategies for the synthesis of ligand-dissymmetric and heterobimetallic macrocycles. The first approach allows one to synthesize bimetallic macrocycles from two distinctly different hemilabile ligands by virtue of sequential addition of the ligands of choice to the appropriate metal precursor (Scheme 6). The second strategy is based on the difference in lability between metal-sulfur and metal-oxygen bonds. Due to the relative differences in binding strengths of



Scheme 6. Synthesis of ligand-dissymmetric macrocycles.

Scheme 7. Synthesis of heterobimetallic macrocycles.

these weakly binding groups towards late transition metals, heterobimetallic macrocyclic intermediates can be synthesized in chemoselective fashion with Rh(I) and Pd(II) placed in either coordination pocket (Scheme 7). The weak bonds in these intermediates can be sequentially broken through ligand substitution reactions to generate fully or partially open macrocyclic architectures that could provide new pathways for mixed-metal cooperative catalysis or allosteric control of cavity size and shape.

Significantly, these strategies provide entry into a new class of macrocycles with tailorabile choice of metal centers and hemilabile ligand backbones. In particular, both ligand-dissymmetric and heterobimetallic macrocycles contain a diverse set of weak metal-ligand bonds that react in different, yet distinct, manners. This distinction provides a route to: (1) the synthesis of complex architectures and arrays by providing selectivity to the incoming bridging ligands, and (2) manipulate the size, shape and charge of the macrocyclic cavity through step-wise reaction schemes.

Three-fold Symmetric and Highly Fluorescent Metallacyclic Receptors via The “Weak-Link Approach”. Towards the expansion of this research to novel ligand systems and the fundamental understanding of how the hemilabile ligands direct the formation of these macrocyclic receptors for guest analytes of interest to the DoD that fit within the predefined molecular architecture, we have made advances in generalizing this synthetic approach. For example, we synthesized a three-fold symmetric Rh(I) macrocycle $[\{\text{TPB}(\text{SCH}_2\text{CH}_2\text{PPh}_2)_3\}_2\text{Rh}_3]^{+3}$ (**15**) (TPB = 1,3,5-triphenylbenzene) (Figure 5) from the appropriately designed hemilabile ligand.

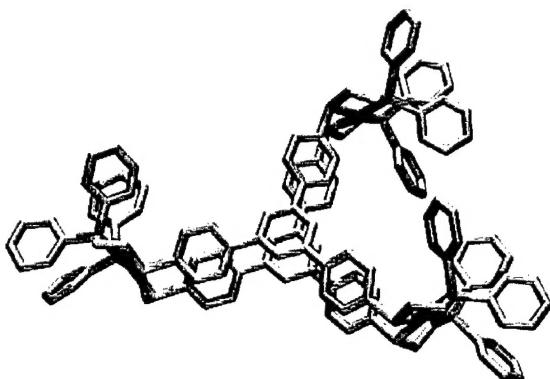


Figure 5. X-Ray structure of complex 15.

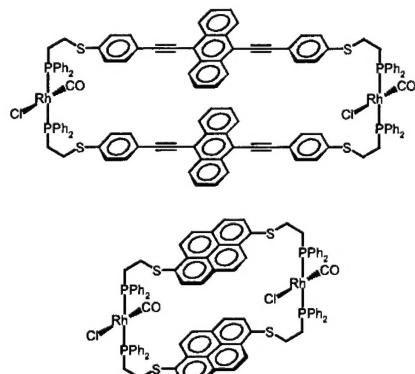


Figure 6. Examples of highly fluorescent macrocyclic complexes.

We also demonstrated the applicability of the “Weak-Link Approach” and hemilabile ligands for the synthesis of new types of highly fluorescent macrocyclic complexes with useful metal-assisted molecular recognition and encapsulating properties for organic molecules (Figure 6). Currently we are investigating their molecular recognition abilities for a variety of polycyclic aromatic molecules. Analytes of particular interest include common environmental pollutants (dioxine, chlorobenzenes) and explosives (TNT, dinitrobenzenes).

These findings are important not only because they provide a high yielding route to large, flexible metallomacrocycles with interesting photophysical and potential molecular recognition properties but also because they provide insight into the basis behind the Weak-Link Approach to macrocycle synthesis and demonstrate the viability of this approach for preparing structures other than bimetallic macrocycles. These results also suggest that our approach could be generalized for a wide variety of higher symmetry structures through appropriate hemilabile ligand design. This approach requires fewer steps and results in higher yields than conventional methods based on covalent organic synthesis.

Highly Fluorescent Rh(I) Macrocycles and Their Applications as Sensors for Small Molecules. Recently, we developed a methodology that allows one to synthesize bimetallic macrocycles from two distinctly different hemilabile ligands by virtue of sequential addition of the ligands of choice to the appropriate metal precursor. We successfully applied this methodology for the synthesis of the dissymmetric “open” Rh(I) macrocycle **16** (Figure 7). The ligand chromophores in this macrocycle act as a donor-acceptor pair in Fluorescence Resonance Energy Transfer (FRET). Currently, we are investigating the fundamental photophysical properties of this complex and its derivatives in order to elucidate the factors (such as solvent

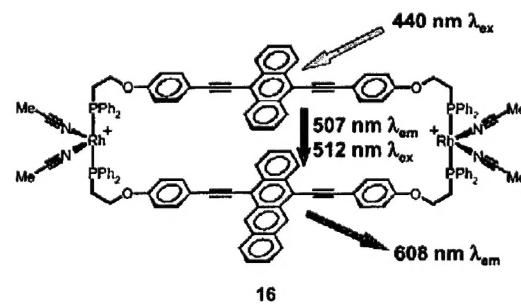


Figure 7. FRET-active macrocycle 16.

and concentration effects, presence of guest molecules capable of filling the internal cavity), which directly influence the effectiveness of FRET processes in these cyclic systems. Also, we are trying to incorporate various hydrophilic ligands ($\text{NCCH}_2\text{CH}_2\text{NMe}_3^+$, $\text{NCCH}_2\text{CH}_2\text{SO}_3^-$) into these open macrocycles in order to probe the molecular sensing capabilities of these complexes in aqueous media. These findings set the stage for the development of a conceptually new type of fast and sensitive technique for monitoring the presence of guest molecules within the confines of “open” macrocycles.

Triptycene-based square metallacycles for molecular recognition of higher fullerenes. We recently synthesized hemilabile ligand **17** (Figure 8) from 1,6-diethynyltriptycene and investigated its reactions with Rh(I) and Pd(II) precursors. The bulky triptycene group in the middle of the ligand **17** and the overall rigid linear geometry of the ligand backbone were adopted to prevent the formation of typical closed bimetallic intermediates. Instead, square tetrametallic macrocycles, *e.g.* complex **18** from the ligand **17**, would be the favorable products in these reactions by virtue of both kinetic and thermodynamic control. The cavity size of the macrocycles of type **18** is estimated to be 14.9 Å. The large cavity size, along with concave triptycene moieties and overall “molecular egg crate” shape, make this macrocycle a promising host for spherical analytes such as C_{70} and the higher fullerenes. The further study of host-guest interactions between Rh(I) macrocycles of type **18** and C_{60} , C_{70} , and mixtures containing higher fullerenes is under way.

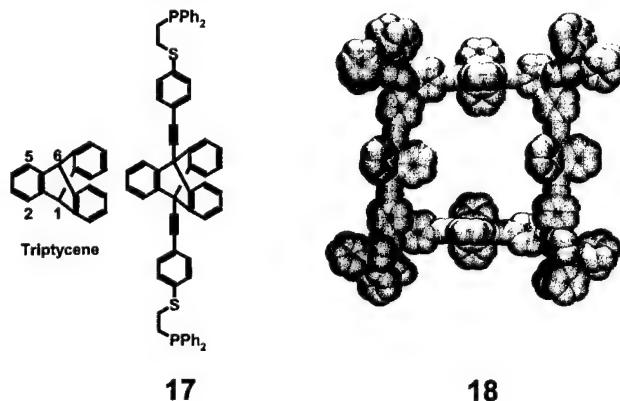


Figure 8. Triptycene based hemilabile ligands **17** and CPK model of square Rh(I) macrocycle **18**.

Writing with multi-component inks. We have recently found that a homogenous mixture of mercaptohexadecanoic acid (MHA) and octadecanethiol (ODT)

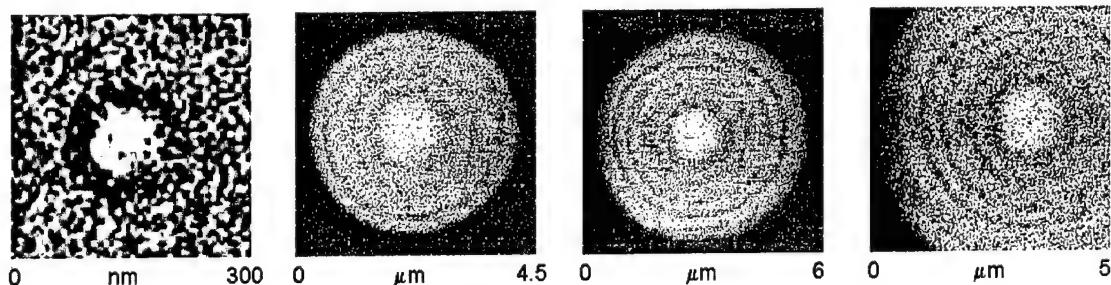
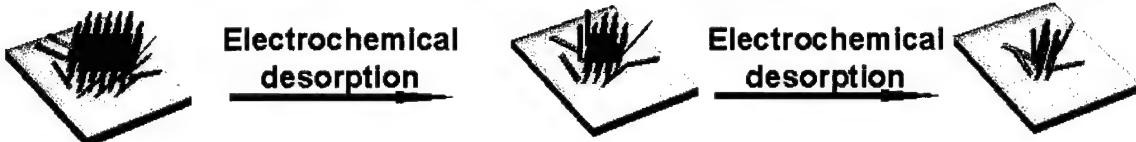


Figure 9. LFM image of phase-separated MHA/ODT ink mixture. **Figure 10.** LFM image of 4 tip approaches to the surface, in which 4 concentric rings can be seen. **Figure 11.** LFM image of 5 tip approaches to the surface, in which 5 concentric rings can be seen. This is the same structure in the previous image, but with an additional approach. **Figure 12.** LFM image of 6 tip approaches to the surface, in which 6 concentric rings can be seen. This is the same structure in the previous image, but with an additional approach.

simultaneously transported to a surface via DPN, will phase separate into two domains. As can be seen from Figure 9, MHA will form a SAM that is clearly separated from the outside ODT SAM. Furthermore, we have observed that multiple tip approaches will form tree ring type structures, with the number of rings representing the number of tip approaches to the surface. Figures 10, 11, and 12 show 4, 5, and 6 approaches respectively. Exploring this phenomenon is imperative for a number of reasons. 1) This is a novel method to study nanoscale phase separation. 2) It provides a tool to study the



Scheme 8. Alkanethiol patterns are whittled away from the edges using the defect sites at the perimeter.

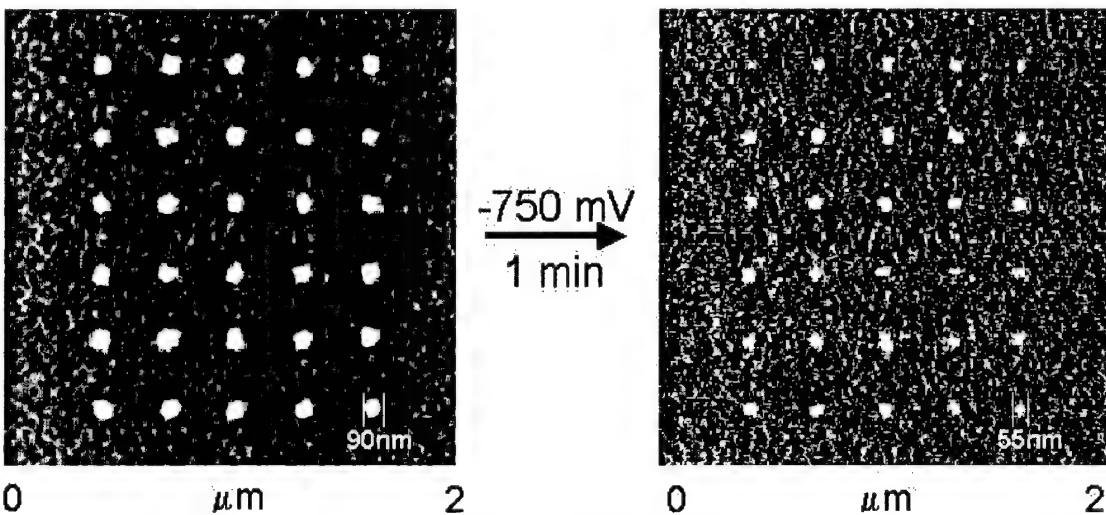
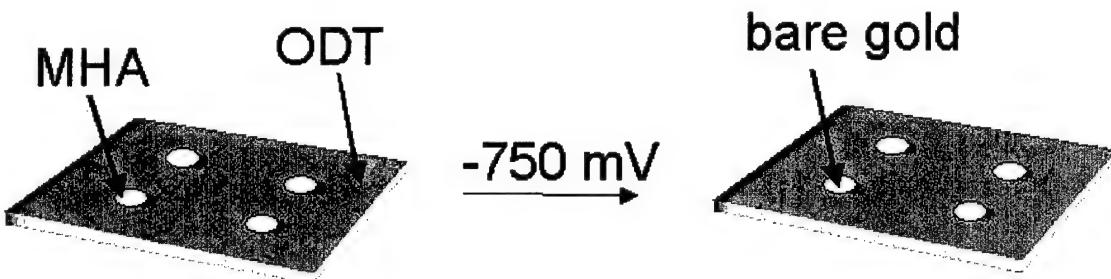


Figure 13. Lateral Force Microscopy (LFM) images of (A) original MHA dots array and (B) the MHA dots array after holding the potential at -750 mV for 1 min. The size of the dots in (A) have been reduced from ~ 90 nm to ~ 55 nm as can be seen in (B).



Scheme 9. Selective desorption of alkanethiol patterns can produce nanoelectrodes of tailorable size.

mechanism of molecular transport through the meniscus, which is central in understanding how DPN works. 3) Varying the tailgroup, chain length and headgroup offers the possibility of engineering electrode surfaces with wettability tailored at the molecular level.

Electrochemical whittling of organic nanostructures. We have recently realized a massively parallel strategy for reducing the size of DPN generated alkanethiol

nanostructures on gold surfaces. This approach works by the electrochemical desorption of organic nanostructures (Scheme 8). For example, by using a conventional three-electrode cell, we were able to reduce the size of DPN patterns from 90 nm to 55nm by applying a potential of -750mV for 1 minute (Figure 13). This phenomena can be explained by the fact that the perimeter of these patterns is rich in defect sites. Therefore, nanostructures are gradually whittled away at a rate dependant on the time and potential applied. This strategy provides a simple and convenient method to instantaneously enhance the resolution of DPN. Also, this method can be used to selectively desorb alkanethiol patters, which provides a convenient method to create nanoelectrodes of tailorable sizes (Scheme 9).

V. Personnel Associated with the Project

All of the HWC undergraduates supported by these funds were minority students: two African-American males, one African-American female, two Hispanic males, and two Hispanic females.

Y01

<u>Project Participant</u>	<u>Status</u>	<u>Salary</u>
Thomas Higgins	HWC Faculty	100% Summer
Chad Mirkin	NU Faculty	3% Summer
Donald Cheatem	HWC Undergraduate Student	100% Summer
Gerri Hutson	HWC Undergraduate Student	100% Summer
Francisco Ruiz	HWC Undergraduate Student	100% Summer
Dr. You-Moon Jeon	NU Post-Doctoral Associate	100% Annual

Y02

<u>Project Participant</u>	<u>Status</u>	<u>Salary</u>
Thomas Higgins	HWC Faculty	100% Summer
Chad Mirkin	NU Faculty	3% Summer
Albert Adebayo	CCC Undergraduate Student	100% Summer
Jacqueline Romero	CCC Undergraduate Student	100% Summer
Xiaogang Liu	NU Graduate Student	25% Annual
Adam Eisenberg	NU Graduate Student	25% Annual
Felicia Dixon*	NU Graduate Student	7% Annual
Dr. You-Moon Jeon	NU Post-Doctoral Associate	100% Annual

*Ms. Dixon received 93% funding from another fellowship (IMIGIP).

Y03

<u>Project Participant</u>	<u>Status</u>	<u>Salary</u>
Thomas Higgins	HWC Faculty	100% Summer
Chad Mirkin	NU Faculty	3% Summer
Jacqueline Romero	CCC Undergraduate Student	100% Annual
Suzanne Arguijo	CCC Undergraduate Student	100% Summer
Arturo Ospina	CCC Undergraduate Student	75% Summer
Adam Eisenberg	NU Graduate Student	100% Annual
Felicia Dixon	NU Graduate Student	100% Annual
Khalid Salaita	NU Graduate Student	100% Annual
Dr. Maxim V. Ovchinnikov	NU Post-Doctoral Associate	100% Annual

VI. PUBLICATIONS

1. Weinberger, D. A.; Hong, S.; Mirkin, C. A.; Wessels, B. W.; Higgins, T. B. "Combinatorial Generation and Analysis of Nano- and Micron Scale Silicon Features Via "Dip-Pen" Nanolithography and Wet Chemical Etching" *Advanced Materials* **2000**, submitted.
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B. Consultative/Advisory Functions

Mirkin consults for and serves on the Scientific Advisory Board and the Board of Directors of both Nanosphere and NanoInk, Inc.

C. Transitions

In addition to several high impact publications that have appeared in print over the last year as a result of this research, this work has been presented and discussed at the fall 2001 222nd and spring 2002 National ACS meeting in Chicago (INORG 0071, 0178, 0179, 0209, 0225, 0225, 0228, 0533, 0534, 0555), 2001 and 2002 Inorganic Gordon Conference, 5th Annual Illinois Minority Graduate Incentive Program Joint Fellows Conference ("Molecular Construction Using Hemilabile Ligands"). The educational activities this proposal has supported include the education and training of several graduate students, post-doctoral fellows and undergraduates, some of which have successfully moved on to prestigious appointments. The graduate students funded by this grant have made significant contributions to the field of supramolecular coordination chemistry and have been able to gain experience presenting this work in both poster and presentation format as a direct result of this funding. The success of this research program has been recognized by several outside funding agencies and internal award committees in the form of fellowship support and teaching awards for several students such as the Committee on Institutional Cooperation/GE Fellowship (Dixon), an Illinois Minority Graduate Incentive Program Fellowship (Dixon).

VI. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

A. New Discoveries

None.

B. New Inventions and/or Patent Disclosures

None.

VII. HONORS/AWARDS

Higgins

- Tenure granted (2000)
- Promotion to Assistant Professor (2000)
- Project Kaleidoscope Faculty for the 21st Century (2000)

Mirkin

- 2004 Nobel Laureate Signature Award for Graduate Education in Chemistry
- Dickinson College Metzger-Conway Fellowship Award (2003)
- 2003 Raymond and Beverly Sackler Prize in the Physical Sciences (NU, 2003)
- Forbes.com, The Forbes/Wolfe Nanotech Report, Mar 2003 “Nanotechnology’s Top 10 Power Brokers”
- 2002 Feynman Prize in Nanotechnology (NU, 2002)
- 2002 Ceramographic Competition, American Ceramic Society 1st Place Entry (NU, 2002)
- Esquire Magazine’s “Best & Brightest in the Nation” (NU, 2002)
- 2001 Leo Hendrick Baekeland Award (NU, 2001)
- Crain’s Chicago Business “40 under 40 Award” (NU, 2001)
- Discover 2000 Award for Technological Innovation (NU, 2000)
- Elected Fellow of the American Association for the Advancement of Science (NU, 2000)
- I-Street Magazine’s Top 5 List for Leading Academics in Technology (NU, 2000)